

DESCRIPTION

Nonaqueous Electrolyte Battery

5 Technical Field

The present invention relates to a nonaqueous electrolyte battery, and more particularly, it relates to a nonaqueous electrolyte battery whose positive electrode active material layer contains a conductive material.

10

Background Technique

In general, a lithium secondary battery is known as a high-capacity nonaqueous electrolyte battery. Such a lithium secondary battery is disclosed in Japanese Patent Laying-Open No. 10-83818, for example. In this conventional lithium secondary battery, the capacity of the lithium secondary battery has been increased by increasing the filling density of a positive electrode active material layer (mass per volume of the positive electrode active material layer (excluding the mass of a collector)). More specifically, the capacity per volume of the positive electrode active material layer has been increased by employing a layered rock salt material having a high true density as a positive electrode active material constituting the positive electrode active

15

20

25

material layer. In general, further, only carbon black having a specific resistance of $40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$ has been employed as a conductive material contained in the positive electrode active material layer.

5 In the aforementioned lithium secondary battery as the conventional nonaqueous electrolyte battery, however, there has been such inconvenience that it is difficult to further increase the filling density of the positive electrode active material layer since the true density
10 (2.2 g/ml) of carbon black as the conductive material contained in the positive electrode active material layer is low. Consequently, there has been such a problem that it is difficult to further increase the capacity of the lithium secondary battery (nonaqueous electrolyte battery).
15 Further, there has been such inconvenience that, in a case of setting the dissolution/deposition potential of lithium metal as the reference potential (0 V vs. Li/Li^+), a nonaqueous electrolyte catalyzed by carbon black is decomposed or anions (negative ions) of the electrolyte
20 are doped into carbon black when 4 V is exceeded with respect to the reference potential. In other words, there has been such a problem that the capacity of the lithium secondary battery (nonaqueous electrolyte battery) lowers due to chemical reaction caused on the interfaces between
25 carbon black and the nonaqueous electrolyte as well as the

positive electrode active material under a high voltage
(at least 4 V).

Disclosure of the Invention

5 The present invention has been proposed in order to
solve the aforementioned problems, and an object of the
present invention is to provide a nonaqueous electrolyte
battery capable of more increasing the capacity per volume
of a positive electrode active material layer than a case
10 of employing only carbon black as a conducting material.

 In order to attain the aforementioned object, a
nonaqueous electrolyte battery according to a first aspect
of the present invention comprises a positive electrode
including a positive electrode active material layer, a
15 negative electrode including a negative electrode active
material layer, a nonaqueous electrolyte and a conductive
material, contained in the positive electrode active
material layer, containing carbon black having a specific
surface area of at least $1 \text{ m}^2/\text{g}$ and less than $800 \text{ m}^2/\text{g}$ and
20 at least one material selected from a group consisting of
nitrides, carbides and borides.

 In this nonaqueous electrolyte battery according to
the first aspect, the filling density of the positive
electrode active material layer (mass per volume of the
25 positive electrode active material layer (excluding the

mass of a collector)) can be more increased than a case of employing a conductive material containing only carbon black, by employing the conductive material containing carbon black and at least one material selected from the group consisting of nitrides, carbides and borides as hereinabove described. This is because at least one material selected from the group consisting of nitrides, carbides and borides has a higher true density than carbon black. Thus, it is possible to increase the capacity per volume of the positive electrode active material layer. Further, it is possible to more improve charge/discharge cycle characteristics (capacity retention ratio) than a case of employing a conductive material containing only one material selected from the group consisting of nitrides, carbides and borides. In addition, at least one material selected from the group consisting of nitrides, carbides and borides is a material hardly causing chemical reaction with the nonaqueous electrolyte and a positive electrode active material constituting the positive electrode active material layer under a high voltage (at least 4 V) as compared with carbon black, whereby reduction of the capacity resulting from chemical reaction of at least one material selected from the group consisting of nitrides, carbides and borides can be suppressed. Further, the contact areas on the interfaces

between carbon black and the nonaqueous electrolyte as well as the positive electrode active material constituting the positive electrode active material layer can be reduced by setting the specific surface area of carbon black to at least $1 \text{ m}^2/\text{g}$ and less than $800 \text{ m}^2/\text{g}$, whereby chemical reaction caused on the interfaces between carbon black and the nonaqueous electrolyte as well as the positive electrode active material can be so suppressed that the capacity can be inhibited from reduction as a result. Thus, according to the first aspect, it is possible to increase the capacity of the nonaqueous electrolyte battery and to improve the charge/discharge cycle characteristics while suppressing reduction of the capacity resulting from chemical reaction of the conductive material by employing the conductive material containing carbon black and at least one material selected from the group consisting of nitrides, carbides and borides and setting the specific surface area of carbon black to at least $1 \text{ m}^2/\text{g}$ and less than $800 \text{ m}^2/\text{g}$.

In the aforementioned nonaqueous electrolyte battery according to the first aspect, the conductive material preferably contains the carbon black and the nitride. The true density of the nitride is higher than the true density of carbon black, whereby the capacity per volume of the positive electrode active material layer can be

easily increased. Further, the nitride is a material hardly causing chemical reaction with the nonaqueous electrolyte and the positive electrode active material constituting the positive electrode active material layer under a high voltage (at least 4 V) as compared with carbon black, whereby reduction of the capacity resulting from chemical reaction of the nitride can be easily suppressed.

In the aforementioned nonaqueous electrolyte battery according to the first aspect, the nitride preferably includes a metal nitride. Since the true density (3 g/ml to 17 g/ml) of the metal nitride is higher than the true density (2.2 g/ml) of carbon black, the filling density of the positive electrode active material layer can be easily increased when constituting the conductive material to contain the metal nitride. Further, excellent conductivity can be easily ensured when employing a metal nitride having a specific resistance approximate to the specific resistance ($40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$) of carbon black.

In this case, the metal nitride preferably includes zirconium nitride (ZrN or Zr_3N_2). Since zirconium nitride has a true density of 7 g/ml and a specific resistance of $13.6 \times 10^{-6} \Omega\text{cm}$, it is possible to easily increase the filling density of the positive electrode active material layer while ensuring excellent conductivity. The chemical

formula of zirconium nitride is univocally indeterminable, and assumed to be either ZrN or Zr_3N_2 .

In the aforementioned nonaqueous electrolyte battery according to the first aspect, at least one material selected from the group consisting of nitrides, carbides and borides preferably has particles of at least $0.2\ \mu m$ and not more than $5\ \mu m$ in average particle diameter easily dispersed into the positive electrode active material layer. According to this structure, dispersibility of at least one material selected from the group consisting of nitrides, carbides and borides in the positive electrode active material layer so improves that more excellent conductivity can be ensured.

A nonaqueous electrolyte battery according to a second aspect of the present invention comprises a positive electrode including a positive electrode active material layer, a negative electrode including a negative electrode active material layer, a nonaqueous electrolyte and a conductive material, contained in the positive electrode active material layer, containing carbon black and at least one material, selected from a group consisting of nitrides, carbides and borides, having particles of at least $0.2\ \mu m$ and not more than $5\ \mu m$ in average particle diameter easily dispersed into the positive electrode active material layer.

In this nonaqueous electrolyte battery according to the second aspect, the filling density of the positive electrode active material layer (mass per volume of the positive electrode active material layer (excluding the mass of a collector)) can be more increased than a case of employing a conductive material containing only carbon black, by employing the conductive material containing carbon black and at least one material selected from the group consisting of nitrides, carbides and borides as hereinabove described. This is because at least one material selected from the group consisting of nitrides, carbides and borides has a higher true density than carbon black. Thus, it is possible to increase the capacity per volume of the positive electrode active material layer. Further, it is possible to more improve charge/discharge cycle characteristics (capacity retention ratio) than a case of employing a conductive material containing only one material selected from the group consisting of nitrides, carbides and borides. In addition, at least one material selected from the group consisting of nitrides, carbides and borides is a material hardly causing chemical reaction with the nonaqueous electrolyte and a positive electrode active material constituting the positive electrode active material layer under a high voltage (at least 4 V) as compared with carbon black, whereby

reduction of the capacity resulting from chemical reaction of at least one material selected from the group consisting of nitrides, carbides and borides can be suppressed. Further, at least one material selected from the group consisting of nitrides, carbides and borides is so constituted as to have the particles of at least 0.2 μm and not more than 5 μm in average particle diameter easily dispersed into the positive electrode active material layer that dispersibility of at least one material selected from the group consisting of nitrides, carbides and borides in the positive electrode active material layer improves, whereby excellent conductivity can be ensured. Thus, according to the second aspect, it is possible to increase the capacity of the nonaqueous electrolyte battery and to improve the charge/discharge cycle characteristics while suppressing reduction of conductivity of the positive electrode active material layer and reduction of the capacity resulting from chemical reaction of the conductive material by employing the conductive material containing carbon black and at least one material selected from the group consisting of nitrides, carbides and borides and constituting at least one material selected from the group consisting of nitrides, carbides and borides to have the particles of at least 0.2 μm and not more than 5 μm in average particle

diameter easily dispersed into the positive electrode active material layer.

In the aforementioned nonaqueous electrolyte battery according to the second aspect, the conductive material preferably contains the carbon black and the nitride. The true density of the nitride is higher than the true density of carbon black, whereby the capacity per volume of the positive electrode active material layer can be easily increased. Further, the nitride is a material hardly causing chemical reaction with the nonaqueous electrolyte and the positive electrode active material constituting the positive electrode active material layer under a high voltage (at least 4 V) as compared with carbon black, whereby reduction of the capacity resulting from chemical reaction of the nitride can be easily suppressed.

In the aforementioned nonaqueous electrolyte battery according to the second aspect, the nitride preferably includes a metal nitride. Since the true density (3 g/ml to 17 g/ml) of the metal nitride is higher than the true density (2.2 g/ml) of carbon black, the filling density of the positive electrode active material layer can be easily increased when constituting the conductive material to contain the metal nitride. Further, excellent conductivity can be easily ensured when employing a metal nitride

having a specific resistance approximate to the specific resistance ($40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$) of carbon black.

In this case, the metal nitride preferably includes zirconium nitride (ZrN or Zr_3N_2). Since zirconium nitride
5 has a true density of 7 g/ml and a specific resistance of $13.6 \times 10^{-6} \Omega\text{cm}$, it is possible to easily increase the filling density of the positive electrode active material layer while ensuring excellent conductivity. The chemical formula of zirconium nitride is univocally indeterminable,
10 and assumed to be either ZrN or Zr_3N_2 .

In the aforementioned nonaqueous electrolyte battery according to the second aspect, the carbon black preferably has a specific surface area of at least $1 \text{ m}^2/\text{g}$ and less than $800 \text{ m}^2/\text{g}$. According to this structure, the
15 contact areas on the interfaces between carbon black and the nonaqueous electrolyte as well as the positive electrode active material constituting the positive electrode active material layer can be reduced, whereby chemical reaction caused on the interfaces between carbon
20 black and the nonaqueous electrolyte as well as the positive electrode active material can be suppressed. Thus, the capacity can be further inhibited from reduction.

A nonaqueous electrolyte battery according to a third aspect of the present invention comprises a positive
25 electrode including a positive electrode active material

layer, a negative electrode including a negative electrode active material layer, a nonaqueous electrolyte and a conductive material, contained in the positive electrode active material layer, containing carbon black having a specific surface area of at least 1 m²/g and less than 800 m²/g and zirconium nitride (ZrN or Zr₃N₂) having particles of at least 0.2 μm and not more than 5 μm in average particle diameter easily dispersed into the positive electrode active material layer.

In this nonaqueous electrolyte battery according to the third aspect, the filling density of the positive electrode active material layer (mass per volume of the positive electrode active material layer (excluding the mass of a collector)) can be more increased than a case of employing a conductive material containing only carbon black, by employing the conductive material containing carbon black and zirconium nitride as hereinabove described. This is because zirconium nitride has a higher true density than carbon black. Thus, it is possible to increase the capacity per volume of the positive electrode active material layer. Further, it is possible to more improve charge/discharge cycle characteristics (capacity retention ratio) than a case of employing a conductive material containing only zirconium nitride. In addition, zirconium nitride is a material hardly causing chemical

reaction with the nonaqueous electrolyte and a positive electrode active material constituting the positive electrode active material layer under a high voltage (at least 4 V) as compared with carbon black, whereby

5 reduction of the capacity resulting from chemical reaction of zirconium nitride can be suppressed. Further, zirconium nitride is so constituted as to have the particles of at least 0.2 μm and not more than 5 μm in average particle diameter easily dispersed into the positive electrode
10 active material layer that dispersibility of zirconium nitride in the positive electrode active material layer improves, whereby excellent conductivity can be ensured.

In addition, the contact areas on the interfaces between carbon black and the nonaqueous electrolyte as well as the
15 positive electrode active material constituting the positive electrode active material layer can be reduced by setting the specific surface area of carbon black to at least 1 m^2/g and less than 800 m^2/g , whereby chemical

reaction caused on the interfaces between carbon black and
20 the nonaqueous electrolyte as well as the positive electrode active material can be so suppressed that the capacity can be inhibited from reduction as a result. Thus, according to the third aspect, it is possible to increase the capacity of the nonaqueous electrolyte battery and to
25 improve the charge/discharge cycle characteristics while

suppressing reduction of conductivity of the positive electrode active material layer and reduction of the capacity resulting from chemical reaction of the conductive material by employing the conductive material containing carbon black having the specific surface area of at least $1 \text{ m}^2/\text{g}$ and less than $800 \text{ m}^2/\text{g}$ and zirconium nitride having the particles of at least $0.2 \text{ }\mu\text{m}$ and not more than $5 \text{ }\mu\text{m}$ in average particle diameter easily dispersed into the positive electrode active material layer.

Brief Description of the Drawings

[Fig. 1] Fig. 1 is a graph showing particle size distribution of zirconium nitride constituting a conductive material employed in Example 1.

[Fig. 2] Fig. 2 is an SEM (Scanning Electron Microscope: scanning electron microscope) photograph of zirconium nitride constituting the conductive material employed in Example 1.

[Fig. 3] Fig. 3 is a perspective view showing a test cell prepared for checking the characteristics of positive electrodes of lithium secondary batteries (nonaqueous electrolyte batteries) according to Examples 1 to 3, comparative example 1 and comparative example 2.

[Fig. 4] Fig. 4 is a graph showing results of a

charge/discharge test performed as to a test cell
corresponding to Example 1.

[Fig. 5] Fig. 5 is a graph showing results of a
charge/discharge test performed as to a test cell
5 corresponding to Example 2.

[Fig. 6] Fig. 6 is a graph showing results of a
charge/discharge test performed as to a test cell
corresponding to Example 3.

[Fig. 7] Fig. 7 is a graph showing results of a
10 charge/discharge test performed as to a test cell
corresponding to comparative example 1.

[Fig. 8] Fig. 8 is a graph showing results of a
charge/discharge test performed as to a test cell
corresponding to comparative example 2.

15

Best Modes for Carrying Out the Invention

Examples of the present invention are now
specifically described.

(Example 1)

20

[Preparation of Positive Electrode]

According to this Example 1, a conductive material
containing carbon black having a specific surface area of
12 m²/g and zirconium nitride having particles of at least
0.2 μm and not more than 5 μm in average particle diameter
25 easily dispersed into a positive electrode active material

layer was employed as the conductive material constituting the positive electrode active material layer. Carbon black has a true density of 2.2 g/ml and a specific resistance of $40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$, while zirconium nitride has a true density of 7 g/ml and a specific resistance of $13.6 \times 10^{-6} \Omega\text{cm}$. Lithium cobaltate (LiCoO_2) and polyvinylidene fluoride (PVdF) were employed as a positive electrode active material and a binder constituting the positive electrode active material layer respectively. Lithium cobaltate has a layered rock salt structure and a true density of 5 g/ml.

Particle size distribution measurement was performed in order to check the specific average particle diameter of zirconium nitride constituting the conductive material employed in Example 1. A laser diffraction particle size distribution measuring apparatus (SALD-2000, by Shimadzu Corporation) was employed for the particle size distribution measurement. The average particle diameter is a median diameter measured with the laser diffraction particle size distribution measuring apparatus.

Fig. 1 shows the particle size distribution of zirconium nitride constituting the conductive material employed in Example 1. The particle diameter (μm) is plotted on the abscissa of Fig. 1. Further, the relative particle quantity (%) is plotted on the left ordinate of

Fig. 1, and shown by a curvilinear graph. Frequency distribution (%) is plotted on the right ordinate of Fig. 1, and shown by a bar graph. The relative particle quantity is the proportion of particles of not more than a prescribed particle diameter with respect to the overall particle quantity. The frequency distribution is the proportion of particles present in each particle diameter range with respect to the overall particle quantity when the range of the particle diameters is divided at regular intervals. The mode diameter in Fig. 1 is the particle diameter of particles maximumly present in the measured object.

Referring to Fig. 1, the average particle diameter (median diameter) of zirconium nitride constituting the conductive material employed in Example 1 is $3.1\text{ }\mu\text{m}$, and it has been confirmable that the average particle diameter is at least $0.2\text{ }\mu\text{m}$ and not more than $5\text{ }\mu\text{m}$. Further, the mode diameter is $3.8\text{ }\mu\text{m}$, and it has been confirmable that the particles having particle diameters of at least $0.2\text{ }\mu\text{m}$ and not more than $5\text{ }\mu\text{m}$ are maximumly present.

Referring to Fig. 2, it has been proved that particles of zirconium nitride constituting the conductive material employed in Example 1 homogeneously disperse over the whole. From this result, it is conceivable that dispersibility of the particles improves when the average

particle diameter of zirconium nitride is at least 0.2 μm and not more than 5 μm .

Then, the aforementioned materials constituting the positive electrode active material layer were mixed with each other so that the mass ratios of lithium cobaltate (positive electrode active material), carbon black (conductive material), zirconium nitride (conductive material) and polyvinylidene fluoride (binder) were 94:1:2:3. Then, N-methyl-2-pyrrolidone was added to this mixture for preparing a positive electrode mixture slurry as the positive electrode active material layer. Finally, the positive electrode mixture slurry as the positive electrode active material layer was applied onto aluminum foil as a collector, and the collector and the positive electrode active material layer were thereafter cut into quadratic forms 2 cm square, thereby preparing a positive electrode of a lithium secondary battery (nonaqueous electrolyte battery) according to Example 1. According to Example 1, the filling density of the positive electrode active material layer (mass per volume of the positive electrode active material layer) constituting the positive electrode was 4.13 g/ml. The filling density of the positive electrode active material layer in the present invention is that exclusive of the aluminum foil as the collector.

(Example 2)

[Preparation of Positive Electrode]

According to this Example 2, a conductive material containing carbon black having a specific surface area of 39 m²/g and zirconium nitride having particles of at least 0.2 μm and not more than 5 μm in average particle diameter easily dispersed into a positive electrode active material layer was employed as the conductive material constituting the positive electrode active material layer. As a result of performing particle size distribution measurement similar to that in the aforementioned Example 1 on zirconium nitride constituting the conductive material, the specific average particle diameter of zirconium nitride was 3.1 μm. As a positive electrode active material layer and a binder constituting the positive electrode active material layer, lithium cobaltate and polyvinylidene fluoride were employed respectively.

Similarly to the aforementioned Example 1, a positive electrode mixture slurry as the positive electrode active material layer was so prepared that the mass ratios of lithium cobaltate (positive electrode active material), carbon black (conductive material), zirconium nitride (conductive material) and polyvinylidene fluoride (binder) were 94:1:2:3. Finally, the positive electrode mixture slurry as the positive electrode active material layer was

applied onto aluminum foil as a collector, and the collector and the positive electrode active material layer were thereafter cut into quadratic forms 2 cm square, thereby preparing a positive electrode of a lithium secondary battery (nonaqueous electrolyte battery) according to Example 2. According to Example 2, the filling density of the positive electrode active material layer constituting the positive electrode was 4.20 g/m.

(Example 3)

[Preparation of Positive Electrode]

According to this Example 3, a conductive material containing carbon black having a specific surface area of 70 m²/g and zirconium nitride having particles of at least 0.2 μm and not more than 5 μm in average particle diameter easily dispersed into a positive electrode active material layer was employed as the conductive material constituting the positive electrode active material layer. As a result of performing particle size distribution measurement similar to that in the aforementioned Example 1 on zirconium nitride constituting the conductive material, the specific average particle diameter of zirconium nitride was 3.1 μm. As a positive electrode active material layer and a binder constituting the positive electrode active material layer, lithium cobaltate and polyvinylidene fluoride were employed respectively.

The aforementioned materials constituting the positive electrode active material layer were so mixed with each other that the mass ratios of lithium cobaltate (positive electrode active material), carbon black (conductive material), zirconium nitride (conductive material) and polyvinylidene fluoride (binder) were 91:1:5:3. Similarly to the aforementioned Example 1, N-methyl-2-pyrrolidone was added to this mixture for preparing a positive electrode mixture slurry as the positive electrode active material layer. Finally, the positive electrode mixture slurry as the positive electrode active material layer was applied onto aluminum foil as a collector, and the collector and the positive electrode active material layer were thereafter cut into quadratic forms 2 cm square, thereby preparing a positive electrode of a lithium secondary battery (nonaqueous electrolyte battery) according to Example 3. According to Example 3, the filling density of the positive electrode active material layer constituting the positive electrode was 4.16 g/m.

(Comparative Example 1)

[Preparation of Positive Electrode]

According to this comparative example 1, a conductive material containing carbon black having a specific surface area of 800 m²/g and zirconium nitride having an average

particle diameter of 3.1 μm was employed as the conductive material constituting a positive electrode active material layer. As a positive electrode active material layer and a binder constituting the positive electrode active material layer, lithium cobaltate and polyvinylidene fluoride were employed respectively.

Similarly to the aforementioned Example 3, a positive electrode mixture slurry as the positive electrode active material layer was so prepared that the mass ratios of lithium cobaltate (positive electrode active material), carbon black (conductive material), zirconium nitride (conductive material) and polyvinylidene fluoride (binder) were 91:1:5:3. Finally, the positive electrode mixture slurry as the positive electrode active material layer was applied onto aluminum foil as a collector, and the collector and the positive electrode active material layer were thereafter cut into quadratic forms 2 cm square, thereby preparing a positive electrode of a lithium secondary battery (nonaqueous electrolyte battery) according to comparative example 1. According to comparative example 1, the filling density of the positive electrode active material layer constituting the positive electrode was 4.09 g/m.

(Comparative Example 2)

According to this comparative example 2, a conductive

material containing only zirconium nitride of 3.1 μm in average particle diameter was employed as the conductive material constituting a positive electrode active material layer. As a positive electrode active material layer and a binder constituting the positive electrode active material layer, lithium cobaltate and polyvinylidene fluoride were employed respectively.

The aforementioned materials constituting the positive electrode active material layer were so mixed with each other that the mass ratios of lithium cobaltate (positive electrode active material), zirconium nitride (conductive material) and polyvinylidene fluoride (binder) were 87:10:3. Similarly to the aforementioned Example 1, N-methyl-2-pyrrolidone was added to this mixture for preparing a positive electrode mixture slurry as the positive electrode active material layer. Finally, the positive electrode mixture slurry as the positive electrode active material layer was applied onto aluminum foil as a collector, and the collector and the positive electrode active material layer were thereafter cut into quadratic forms 2 cm square, thereby preparing a positive electrode of a lithium secondary battery (nonaqueous electrolyte battery) according to comparative example 2. According to comparative example 2, the filling density of the positive electrode active material layer constituting

the positive electrode was 4.49 g/m.

(Common to Examples 1 to 3, Comparative Example 1 and Comparative Example 2)

[Preparation of Nonaqueous Electrolyte]

5 A nonaqueous electrolyte of the lithium secondary battery (nonaqueous electrolyte battery) was prepared by dissolving 1 mol/liter of lithium hexafluorophosphate (LiPF_6) as an electrolyte (solute) in a mixed solvent obtained by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) at a volume ratio of 50:50.

[Preparation of Test Cell]

Referring to Fig. 3, a positive electrode 1 and a negative electrode 2 were arranged in a vessel 10 so that the positive electrode 1 and the negative electrode 2 were
15 opposed to each other through a separator 3, while a reference electrode 4 was also arranged in the vessel 10 as a preparation process for a test cell. The test cell was prepared by injecting a nonaqueous electrolyte 5 into the vessel 10. A positive electrode prepared in the
20 aforementioned manner was employed as the positive electrode 1, while lithium (Li) metal was employed as the negative electrode 2 and the reference electrode 3. A nonaqueous electrolyte prepared in the aforementioned manner was employed as the nonaqueous electrolyte 5.

25 [Charge/Discharge Test]

Charge/discharge tests were performed as to
respective test cells corresponding to Examples 1 to 3,
comparative example 1 and comparative example 2 prepared
in the aforementioned manner. As to conditions of this
5 charging/discharging, charging was performed up to 4.3 V
with constant current of 1.5 mA, and discharging was
thereafter performed up to 2.75 V with the constant
current of 1.5 mA. This charging/discharging was assumed
to be one cycle, for measuring first-cycle and fourth-
10 cycle post-discharge capacities.

Referring to Figs. 4 to 7, it has been proved that
the first-cycle post-discharge capacities are higher in
Examples 1 to 3 in which the specific surfaces areas of
carbon black constituting the conductive materials are at
15 least 1 m²/g and less than 800 m²/g than comparative
example 1 in which the specific surface area of carbon
black is 800 m²/g. More specifically, the first-cycle
post-discharge capacity of Example 1 (see Fig. 4) in which
the specific surface area of carbon black is 12 m²/g was
20 560 mAh/ml. The first-cycle post-discharge capacity of
Example 2 (see Fig. 5) in which the specific surface area
of carbon black is 39 m²/g was 572 mAh/ml. The first-cycle
post-discharge capacity of Example 3 (see Fig. 6) in which
the specific surface area of carbon black is 70 m²/g was
25 557 mAh/ml. In other words, it was possible to obtain high

capacities (at least 557 mAh/ml) in Examples 1 to 3 after the first-cycle discharging. On the other hand, the first-cycle post-discharge capacity of comparative example 1 (see Fig. 7) in which the specific surface area of carbon black is 800 m²/g was 532 mAh/ml. The capacities (mAh/ml) shown in Figs. 4 to 7 are capacities per volume of the positive electrode active material layers.

From this result, it is conceivable that reduction of the capacities was suppressed in Examples 1 to 3 by setting the specific areas of carbon black constituting the conductive materials to at least 1 m²/g and less than 800 m²/g. In other words, it is conceivable that the contact areas on the interfaces between carbon black and the nonaqueous electrolytes as well as the positive electrode active materials can be reduced by setting the specific areas of carbon black constituting the conductive materials to at least 1 m²/g and less than 800 m²/g, whereby chemical reaction caused on the interfaces between carbon black and the nonaqueous electrolytes as well as the positive electrode active materials can be suppressed and the capacities can be inhibited from reduction as a result.

Referring to Figs. 4 to 6 and Fig. 8, it has been proved that capacity retention ratios (ratios of fourth-cycle post-discharge capacities to first-cycle post-

discharge capacities) more improve in Examples 1 to 3 employing the conductive materials containing carbon black and zirconium nitride than comparative example 2 employing the conductive material containing only zirconium nitride.

5 More specifically, the first-cycle post-discharge capacities of Example 1 (see Fig. 4), Example 2 (see Fig. 5) and Example 3 (see Fig. 6) employing the conductive materials containing carbon black and zirconium nitride were 560 mAh/ml, 572 mAh/ml and 557 mAh/ml respectively, 10 and the fourth-cycle post-discharge capacities were 566 mAh/ml, 567 mAh/ml and 555 mAh/ml respectively. In other words, the capacity retention ratios of Example 1, Example 2 and Example 3 were 100 %, 99.1 % and 99.6 % respectively. In comparative example 2 (see Fig. 8) employing the 15 conductive material containing only zirconium nitride, on the other hand, the first-cycle and fourth-cycle post-discharge capacities were 585 mAh/ml and 553 mAh/ml respectively. In other words, the capacity retention ratio of comparative example 2 was 94.5 %. The capacities 20 (mAh/ml) shown in Fig. 8 are capacities per volume of the positive electrode active material layers.

From this result, it is conceivable that the capacity retention ratios were employed in Examples 1 to 3 due to the employment of the conductive materials containing 25 carbon black and zirconium nitride. In other words, it is

conceivably possible to more improve the charge/discharge cycle characteristics (capacity retention ratios) in Examples 1 to 3 than a case of employing a conductive material containing only zirconium nitride, by employing the conductive materials containing carbon black and zirconium nitride.

It has been proved that the charge/discharge cycle characteristics improve while the first-cycle capacities lower in Examples 1 to 3 as compared with comparative example 2. This is conceivably because the filling density of the positive electrode active material layer was more increased in comparative example 2 employing the conductive material containing only zirconium nitride having the true density (7 g/ml) higher than the true density (2.2 g/ml) of carbon black than Examples 1 to 3 employing the conductive materials containing carbon black and zirconium nitride.

According to Examples 1 to 3, as hereinabove described, it is possible to improve the charge/discharge cycle characteristics while suppressing reduction of the capacities resulting from chemical reaction caused on the interfaces between carbon black and the nonaqueous electrolytes as well as the positive electrode active materials by employing the conductive materials containing carbon black and zirconium nitride and setting the

specific surface areas of carbon black to at least 1 m²/g and less than 800 m²/g.

According to Examples 1 to 3, as hereinabove described, the filling densities of the positive electrode active material layers can be more increased than the case of employing the conductive material containing only carbon black due to the employment of the conductive materials containing carbon black having the true density of 2.2 g/ml and zirconium nitride having the true density of 7 g/ml, whereby the capacities per volume of the positive electrode active material layers can be increased. Further, zirconium nitride is a material hardly causing chemical reaction with a nonaqueous electrolyte and a positive electrode active material under a high voltage (at least 4 V) as compared with carbon black, whereby reduction of the capacities resulting from chemical reaction of zirconium nitride can be suppressed. In addition, dispersibility of zirconium nitride in the positive electrode active material layers can be improved by setting the average particle diameters of zirconium nitride to at least 0.2 μm and not more than 5μm, whereby excellent conductivity can be ensured. Further, the specific resistance ($13.6 \times 10^{-5} \Omega\text{cm}$) of zirconium nitride is approximate to the specific resistance ($40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$) of carbon black, whereby the conductivity is

not reduced due to the employment of the conductive materials containing carbon black and zirconium nitride.

Examples disclosed this time must be considered as illustrative in all points and not restrictive. The scope
5 of the present invention is shown not by the above description of Examples but by the scope of claim for patent, and all modifications within the meaning and range equivalent to the scope of claim for patent are included.

For example, while the examples of applying the
10 present invention to lithium secondary batteries have been described in the above Examples, the present invention is not restricted to this but is also applicable to a nonaqueous electrolyte battery other than the lithium secondary battery.

15 While zirconium nitride was employed as the material constituting the conductive materials with carbon black in the aforementioned Examples, the present invention is not restricted to this but similar effects can be attained also when employing at least one material selected from a
20 group consisting of nitrides other than zirconium nitride, carbides and borides. As a metal nitride other than zirconium nitride, at least one material selected from a group consisting of NbN, TiN, Ti₃N₄, VN, Cr₂N, Fe₂N, Cu₃N, GaN, Mo₂N, Ru₂N, TaN, Ta₂N, HfN, ThN₂, Mo₂N, Mn₃N₂, Co₃N₂,
25 Ni₃N₂, W₂N and Os₂N can be listed, for example. Among the

aforementioned metal nitrides, TiN, Ti₃N₄, TaN and Ta₂N have specific resistances approximate to the specific resistance ($40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$) of carbon black, whereby it is possible to ensure more excellent

5 conductivity when employing TiN, Ti₃N₄, TaN or Ta₂N. The specific resistances of TiN and Ti₃N₄ are $21.7 \times 10^{-6} \Omega\text{cm}$, and the specific resistances of TaN and Ta₂N are $200 \times 10^{-6} \Omega\text{cm}$.

While zirconium nitride having the specific
10 resistance ($13.6 \times 10^{-6} \Omega\text{cm}$) approximate to the specific resistance ($40 \times 10^{-6} \Omega\text{cm}$ to $70 \times 10^{-6} \Omega\text{cm}$) of carbon black was employed as the material constituting the conductive materials with carbon black in the aforementioned Examples, the present invention is not restricted to this but a
15 material inferior in conductivity as compared with carbon black may be employed as the conducting material if it is possible to increase the filling density of the positive electrode active material layer.

While zirconium nitride having the average particle
20 diameter of 3.1 μm was employed as the material constituting the conductive materials with carbon black in the aforementioned Examples, the present invention is not restricted to this but similar effects can be attained when the average particle diameter of zirconium nitride is
25 at least 0.2 μm and not more than 5 μm . If the average

particle diameter of zirconium nitride exceeds 5 μm , it is conceivably rendered difficult to ensure excellent conductivity since dispersion of the conductive material is conceivably inhomogenized to reduce the dispersibility.

5 If the average particle diameter of zirconium nitride is smaller than 0.2 μm , on the other hand, it is conceivably rendered difficult to ensure sufficient conductivity since the contact area between conductive materials contained in the positive electrode active material layer decreases.

10 While the components of the positive electrode active material layers were so mixed with each other that the mass ratios of zirconium nitride constituting the conductive materials were 2 % (Examples 1 and 2) and 5 % (Example 3) in the aforementioned Examples, the present
15 invention is not restricted to this but the mass ratio of zirconium nitride may simply be at least 0.1 % and not more than 5 %. It is more preferable if the mass ratio of zirconium nitride is at least 0.1 % and not more than 3 %, and it is further preferable if the same is at least 0.1 %
20 and not more than 2 %.

While the components of the positive electrode active material layers were so mixed with each other that the mass ratios of carbon black constituting the conductive materials were 1 % in the aforementioned Examples, the
25 present invention is not restricted to this but the mass

ratio of carbon black may simply be not more than 3 %. It is more preferable if the mass ratio of carbon black is not more than 2 %, and it is further preferable if the same is not more than 1 %.

5 While lithium cobaltate (LiCoO_2) was employed as the positive electrode active materials in the aforementioned Examples, the present invention is not restricted to this but a material other than lithium cobaltate may be employed as the positive electrode active material if it is possible to occlude and discharge lithium. As materials
10 other than lithium cobaltate employable as positive electrode active materials, oxides having tunnel holes such as Li_2FeO_3 , TiO_2 and V_2O_5 which are inorganic compounds and metallic chalcogen compounds having layered structures
15 such as TiS_2 and MoS_2 , for example. As the positive electrode active material, it is more preferable to employ a composite oxide having a composition formula expressed as Li_xMO_2 ($0 \leq x \leq 1$) or $\text{Li}_y\text{M}_2\text{O}_4$ ($0 \leq y \leq 2$). M in the composition formula is a transition element. As composite
20 oxides having the aforementioned composition formula, LiMnO_2 , LiNiO_2 , LiCrO_2 and LiMn_2O_4 can be listed, for example. Further, a partial substitute of the Li site and a partial substitute of the transition metal may also be employed.

25 While the nonaqueous electrolytes containing the

mixed solvents of ethylene carbonate and diethyl carbonate were employed in the aforementioned Examples, the present invention is not restricted to this but a solvent other than the mixed solvent of ethylene carbonate and diethyl carbonate may be employed if the same is usable as the solvent of the nonaqueous electrolyte battery. As solvents other than the mixed solvent of ethylene carbonate and diethyl carbonate, cyclic carbonic acid ester, chain carbonic acid ester, esters, cyclic ethers, chain ethers, nitriles and amides can be listed, for example. As cyclic carbonic acid ester, propylene carbonate and butylene carbonate can be listed, for example. Further, cyclic carbonic acid ester whose hydrogen groups are partially or entirely fluorinated is also usable, and trifluoropropylene carbonate and fluoroethyl carbonate can be listed, for example. As chain carbonic acid ester, dimethyl carbonate, ethyl methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate and methyl isopropyl carbonate can be listed, for example. Chain carbonic acid ester whose hydrogen groups are partially or entirely fluorinated is also usable.

As esters, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate and γ -butyrolactone can be listed, for example. As cyclic ethers, 1,3-dioxolane, 4-methyl-1,3-dioxolane, tetrahydrofuran, 2-

methylnetetrahydrofuran, propylene oxide, 1,2-butylene oxide, 1,4-dioxane, 1,3,5-trioxane, furan, 2-methylfuran, 1,8-cineol and crown ether can be listed. As chain ethers, 1,2-dimethoxyethane, diethyl ether, dipropyl ether, 5 diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl ether, butyl phenyl ether, benzyl phenyl ether, methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, 0-dimethoxy benzene, 1,2-diethoxyethane, 10 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether and tetraethylene glycol dimethyl can be listed, for example. As nitriles, 15 acetonitrile can be listed, for example. As amides, dimethylformamide can be listed, for example.

While the nonaqueous electrolytes in which lithium hexafluorophosphate (LiPF_6) as the solute (electrolytic salt) was dissolved were employed in the aforementioned 20 Examples, the present invention is not restricted to this but a nonaqueous electrolyte in which a solute other than lithium hexafluorophosphate is dissolved may be employed. As solutes other than lithium hexafluorophosphate, lithium difluoro(oxalate)borate (substance expressed in the 25 following chemical formula Chem 1), LiAsF_6 , LiBF_4 , LiCF_3SO_3 ,

$\text{LiN}(\text{C}_1\text{F}_{21+1}\text{SO}_2)(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$ and

$\text{LiC}(\text{C}_p\text{F}_{2p+1}\text{SO}_2)(\text{C}_q\text{F}_{2q+1}\text{SO}_2)(\text{C}_r\text{F}_{2r+1}\text{SO}_2)$ can be listed, for

example. l, m, p, q and r in the above composition

formulas are integers of at least 1. Further, a mixture

5 obtained by combining at least two materials selected from

the group consisting of the aforementioned solutes may be

employed as the solute. The aforementioned solute is

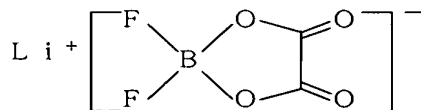
preferably dissolved in the solvent with a concentration

of 0.1 M to 1.5 M. Further, the aforementioned solute is

10 more preferably dissolved in the solvent with a

concentration of 0.5 M to 1.5 M.

Chem 1



While the lithium metal was employed as the negative

15 electrodes in the aforementioned Examples, the present

invention is not restricted to this but a material other

than the lithium metal may be employed as a negative

electrode active material if it is possible to occlude and

discharge lithium. As materials employable as negative

20 electrode active materials, carbon materials such as a

lithium alloy and graphite and silicon can be listed, for

example. Since silicon has a high capacity, a nonaqueous

electrolyte battery of a high energy density can be

obtained when employing a negative electrode containing a negative electrode active material constituted of silicon. This is disclosed in International Patent Laying-Open No. WO01/29912, for example. When forming a negative electrode active material layer on a collector, it is preferable to employ a surface-roughened collector. Further, it is preferable to form the negative electrode active material layer to be columnar. In addition, it is preferable to form the negative electrode active material layer so that the components of the collector are dispersed therein. When forming the negative electrode active material layer in this manner, it is possible to improve the charge/discharge characteristics of the nonaqueous electrolyte battery.

15